Bull. Environ. Contam. Toxicol. (2004) 73:24–30

DOI: 10.1007/s00128-004-0388-y

Bulletin of Environmental Contamination and Toxicology

Evaluation of the Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) Approach to Pesticide Residue Analysis

F. J. Schenck, J. E. Hobbs

Southeast Regional Laboratory, U.S. Food and Drug Administration, 60 Eighth Street NE, Atlanta, GA 30309, USA

Received: 15 October 2003/Accepted: 20 April 2004

Recently, a rapid and inexpensive approach to the analysis of pesticide residues in fruits and vegetables was reported (Anastassiades et al. 2003). The authors named this method QuEChERS, which stands for *Quick, Easy, Cheap, Effective, Rugged and Safe*. Using this method, a batch of 6-12 extracts could be prepared in 20-30 minutes by a single analyst. The QuEChERS method entails extracting the pesticide residues from 10 g of sample by vortex mixing with 10 mL of acetonitrile. No mechanical homogenizers or blenders are used. Water is removed from the extract by salting out with sodium chloride and magnesium sulfate and a subsequent cleanup of the acetonitrile extract is performed by vortexing an aliquot of the extract with a small quantity of solid phase extraction (SPE) sorbent. The authors reported excellent recoveries and repeatabilities for a wide range of fortified pesticides. The QuEChERS method also gave the same results as a traditional method for a sample containing incurred residues.

Using the QuEChERS method for the analysis of pesticides in fresh fruits and vegetables would result in much faster sample analyses, and significant reductions in solvent usage and hazardous waste production. In this study, replicate analyses were performed on 11 samples containing incurred pesticide residues using both the QuEChERS method and the two traditional pesticide residue methods used by Canadian and US Government regulatory agencies. A modified version of the QuEChERS method which allows for lower limits of detection is also presented.

MATERIALS AND METHODS

Pesticide stock standard solutions were prepared from certified neat materials in acetone. Working standard solutions in acetone were prepared from stock solutions. Bulk primary-secondary amine (PSA) SPE sorbent and 500 mg PSA SPE columns were obtained from Varian Sample Preparation Products, Harbor City, CA. Extraction solvent (0.1% acetic acid in acetonitrile) was prepared by adding 1.0 mL glacial acetic acid to 1.0 L acetonitrile.

Gas Chromatography was performed with: 1) HP-5890 Series II® (Hewlett Packard

Correspondence to: F. J. Schenck

Corp., Palo Alto, CA) with: flame photometric detector (FPD); column, 30 m, 1.5 μm, 0.53 mm id, DB-1 widebore capillary (J&W Scientific, Folsom CA), carrier gas UHP Helium, 19 mL/min; Injector 220°C; detector 225°C; oven temperature 130°C for 1 min, 6°C/min, final temperature 275°C; 2) Model 540 gas chromatograph (Tremetrics Inc, Austin, TX) with: Hall electrolytic conductivity detector (HELCD); column, 30 m, 1.5 μm, 0.53 mm id, DB-1 widebore capillary (J&W Scientific); temperature 200°C.; carrier gas UHP Helium, 20 mL/min; make-up gas UHP helium, 10 mL/min. Injector 225°C; reactor base 250°C; reactor furnace 900°C; reactor gas, UHP hydrogen, 60 mL/min.; solvent, n-propanol 0.3 mL/min.

Liquid Chromatography was performed with a Model 1100 HPLC Quaternary pump and Model G1313A autoinjector and a Model G1321A fluorescence detector set at λ= 340 nm, 455nm (Agilent Technologies, Wilmington DE); a Model PCX 5200 postcolumn reaction module (Pickering Laboratories, Mountain View CA); a 4.6 x 250 mm Hypersil Green C_8 column (Alltech Corp., Deerfield IL) operated at 42°C. Injection volume was 10 μL. The mobile phase was 12% acetonitrile/water, linear gradient to 70% acetonitrile/water over 30 min; hold at 70% for 10 minutes; flow 1.0 mL/min.

Domestic and imported produce samples were collected as part of the FDA pesticide residue sampling plan. The samples were homogenized with a Hobart vertical cutter mixer or a Robot Coupe batch food processor with S-blade. Three one pound portions of the resulting sample composite were placed into three containers and stored in a freezer at -20°C. Four portions of sample composite, two from one container and one from each of the other two containers, were analyzed by the QuEChERS method as follows. Sample (10.0 g) was weighed into a 50 mL disposable polypropylene centrifuge tube, 10.0 mL of extraction solvent was added, the tube was capped and vortex mixed for one minute. $MgSO_4$ (4g) and NaCl (1 g) were added to the centrifuge tube and the tube was again vortexed for 1 min. and centrifuged at 1000 rpm. A 5.0 mL aliquot of the supernatant was transferred into a 15 mL glass centrifuge tube. $MgSO_4$ (300 mg) and PSA SPE sorbent (125 mg) were added to the tube and it was vortexed for 30 s and centrifuged briefly. The acetonitrile extract contained 1.0 g sample equivalent per mL of final extract.

During the first part of the study a portion of the acetonitrile extract was transferred to an autosampler vial and injected into a GC equipped with a flame photometric detector. Acetonitrile extract cannot be injected onto a GC equipped with an HELCD. Later in the study the following modifications to the method were made to both increase the sensitivity of the method and permit the use of HELCD detection. Exactly 2.5 mL of the acetonitrile extract was transferred to a second 15 mL centrifuge tube and evaporated under a stream of nitrogen to ca. 0.5 mL. Acetone (10 mL) was added and the solvent was evaporated to ca. 0.5 mL under a stream of nitrogen. The final volume was adjusted to 0.5 mL with acetone, resulting in 5.0 g sample equivalent/mL extract.

At the same time that the QuEChERS extraction was performed, either one or four 50 g portions of sample were analyzed by the method of Fillion at al. (2000) and one 100 g portion of sample was analyzed by the method of Luke et al (1975). Briefly, for the Fillion method, the sample was blended with 100 mL of acetonitrile, the extract was filtered, and the water was separated from the acetonitrile by salting out. An aliquot of acetonitrile extract equivalent to 10 g of product was concentrated to 1.0 mL and eluted through a PSA SPE column with 10 mL of acetone. Briefly for the Luke method, the sample was blended with 200 mL of acetone, and filtered. A 40 mL portion of the aqueous acetone extract was subjected multiple solvent partition cleanups. The extract thus obtained was reduced to < 1 mL, and the extract was eluted through a PSA SPE column with 10 mL of acetone. The final volumes of the Fillion and Luke extracts were adjusted with acetone to give approximate equivalent sample concentrations in the extract of either 1.0 or 5.0 g sample equivalent per mL of final extract.

The Quechers, Luke and Fillion extracts were injected into a GC and/or an LC, depending on the type of pesticide residue(s) present. An LC equipped with a fluorescence detector was used for the carbamate pesticide, carbaryl. A GC equipped with an HELCD was used for organochlorine pesticides such as the three endosulfans, while a GC equipped with an FPD was used for the organophosphorus pesticides.

RESULTS AND DISCUSSION

The QuEChERS method entails extracting 10 g of produce with 10 mL of acetonitrile by vortex mixing. Homogenizers or blenders are not used. Water is subsequently removed from the extract by salting out with sodium chloride and magnesium sulfate. Acetic acid (0.1%) is added to the acetonitrile because certain alkaline-sensitive pesticides were found to be only briefly stable in acetonitrile extracts of samples with a pH of 6-7, but they were stable for more than a day in the acetonitrile extracts containing 0.05% to 0.1% acetic acid (Anastassiades et al. 2003).

The concentrated acetonitrile extracts thus obtained contain many sample matrix coextractants, which results in sample matrix enhancement and damage the capillary GC columns. Recent studies have shown that an efficient cleanup of acetonitrile or acetone extracts can be obtained using a single primary secondary amine (PSA) or aminopropyl (amino) SPE column (Schenck and Lehotay 2002), and that this cleanup will result in significant reductions of the matrix enhancement effect (Schenck and Lehotay 1999). The QuEChERS method uses a cleanup procedure called dispersive SPE. This cleanup entails vortexing an aliquot of the acetonitrile extract with a small quantity of PSA SPE sorbent and magnesium sulfate, rather than eluting the extract through a PSA SPE column.

Eleven different produce samples which contained incurred pesticide residues were analyzed using the QuEChERS method and the two traditional pesticide regulatory

methods. The first set of samples analyzed entailed using the QuEChERS method as originally proposed, i.e. injecting an acetonitrile sample extract containing 1.0 g sample equivalent/mL. The results are shown in Table 1. The method for pesticides in produce, found in both the FDA Pesticide Analytical Manual (McMahon and Wagner 1994) and in the Official Methods of Analysis of AOAC International (Parfitt 2000) suggests an extract containing ca. 4.0 g sample equivalent per mL of

Table 1. Comparison of analytical results obtained using the QuEChERS method and two regulatory methods (QuEChERS extracts contained 1.0 mg sample equivalent/μL injected).

	ppm residue found (% C.V.)		
	Luke[1]	Fillion	QuEChERS[2]
Azinphos methyl			
peach	0.108	0.155(12)[2]	0.177(4.4)
Carbaryl			
green beans	0.264	0.269(1.6)[2]	0.252(1.5)
peach	0.201	0.215 (1.7)[2]	0.198(1.6)
Dimethoate			
snow peas	0.072	0.092[1]	0.085(8.9)
Methamidophos			
Pepper	0.076	0.082(12)[2]	0.096(3.6)
snow peas	0.721	0.741[1]	0.758(10)
Phosmet			
peach	0.537	0.478[1]	0.567(16)
peach	0.246	0.315(9.2)[2]	0.364(4.4)
peach	0.105	0.105(10)[2]	0.105(3.9)

[1]n=1
[2]n=4, values in parentheses are % coefficient of variation.

Table 2. Comparison of analytical results obtained using a modification of the QuEChERS method and two regulatory methods. (QuEChERS extracts contained 5 mg sample equivalent/μL injected).

		ppm residue found (% C.V.)		
		Luke[1]	Fillion[2]	QuEChERS[2]
Chlorpyriphos	snow peas	0.018	0.021(16)	0.017(17)
Dimethoate	snow peas	0.011	0.013(12)	0.011(8.5)
Endosulfan-I	cabbage	0.024	0.020(2.7)	0.017(13)
Endosulfan-II	cabbage	0.017	0.018(11)	0.015(8.0)
Endosulfan SO_4	cabbage	0.053	0.073(7.1)	0.051(9.0)
Methamidophos	snow peas	0.011	0.012(7.6)	0.011(8.1)
Omethoate	snow peas	0.007	0.009(3.9)	0.008(14)
Phosmet	apple	0.039	0.030(16)	0.034(10)

[1]n=1
[2]n=4, values in parentheses are % coefficient of variation.

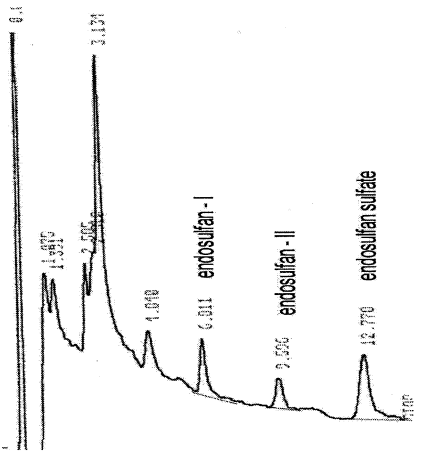

Figure 1. GC chromatograms of a QuEChERS cabbage extract using HELCD detection (0.017, 0.015 and 0.051 ppm endosulfan I, endosulfan II, and endosulfan sulfate).

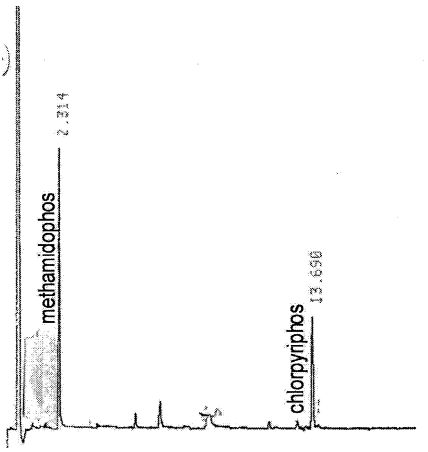

Figure 2. GC chromatogram of QuEChERS snow pea extract using FPD detection (0.010 ppm methamidophos and 0.015 ppm chlorpyriphos).

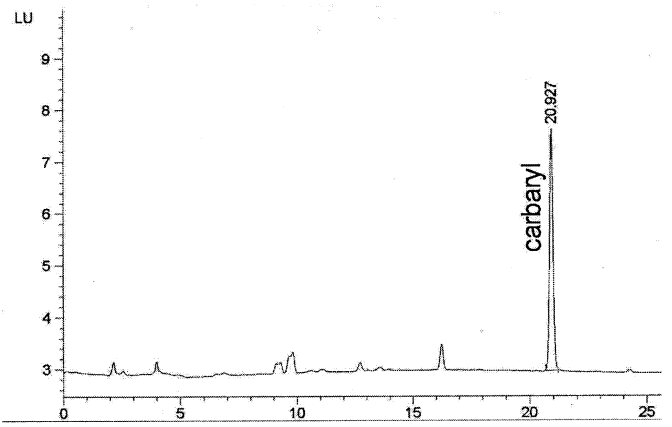

Figure 3. LC-fluorescence chromatogram of QuEChERS peach extract containing 0.196 ppm carbaryl.

extract be used. Another problem with the QuEChERS method is that the acetonitrile solvent would not be compatible with the HELCD detectors used in may laboratories. For the second set of samples, the acetonitrile in the final QuEChERS extract was exchanged to acetone, and the extract was concentrated to 5.0 g sample equivalent/mL. These extracts would be comparable to those obtained using the procedures in the PAM and the AOAC. The results are shown in Table 2.

Initially there were two concerns with the QuEChERS method. The first was whether vortexing with solvent for one minute, rather than using mechanical homogenizers or blenders, would be sufficient to extract the incurred pesticide residues. The second was whether a 10 g sample size would provide a representative sample composite. The results in Tables 1 and 2 show that similar amounts of pesticide residue were found in the samples using the QuEChERS and the two traditional regulatory methods that used mechanical homogenization for the solvent extraction. The results also show that the CVs for the replicate sample analyses, using 10 g and 50 g samples, for the QuEChERS and Fillion methods respectively, were comparable. The incurred residues extracted covered a wide range of polarities, from the nonpolar lipophilic chlorpyriphos to the extremely polar, water soluble methamidophos. With the modification to the QuEChERS method that entails using extracts that contained 5.0 g sample equivalent/ mL, some pesticide residues present at less than 0.010 μg/g (10 parts per billion) could be quantified, as shown in Table 2. Typical chromatograms, using the three types of detection systems, are shown in figures 1-3

The QuEChERS method is a rapid, simple, and inexpensive method that uses minimal amounts of solvent and results in minimal volumes of hazardous waste. The original QuEChERS method was successfully modified, resulting in increased sensitivity and extracts that could be analyzed using HELCD detectors. Similar results were obtained when eleven different produce samples which contained incurred pesticide residues were analyzed using the QuEChERS method and two traditional regulatory methods.

REFERENCES

Anastassiades M, Lehotay SJ, Štajnbaher, D, Schenck, FJ (2002) Fast easy multiresidue method employing acetonitrile extraction partitioning and dispersive solid phase extraction for determination of pesticide residues in produce. J AOAC Int 86:412-431

Fillion J, Sauvé F, Selwyn J (2000) Multiresidue method for the determination of residues of 251 pesticides in fruits and vegetables by gas chromatography/mass spectrometry and liquid chromatography with fluorescence detection. J AOAC Int 83:698-713

Luke MA, Froberg JE, Masumoto HT (1975) Extraction and cleanup of organochlorine, organophosphate, organonitrogen and hydrocarbon pesticides in produce for determination by gas-liquid chromatography. J AOAC Int 58:1020-

1026
McMahon BM, Wagner, RF (1994) Pesticide Analytical Manual. US Food and Drug Administration, Washington DC, section 302
Parfitt CH (2000) Pesticide and industrial chemical residues. In: Horwitz W (ed) Official Methods of Analysis of AOAC International, vol 1. AOAC International, Gaithersburg MD, section 10.1.2
Schenck FJ, Lehotay SJ (2000) Does further clean-up reduce the matrix enhancement effect in gas chromatographic analysis of pesticide residues in food? J Chromatog A 868:51-61
Schenck FJ, Lehotay SJ, Vega V (2002) Comparison of solid-phase extraction sorbents for cleanup in pesticide residue analysis of fresh fruits and vegetables. J Sep Sci 25:10-16